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(54) **Automatic dishwashing compositions**

(57) The use of water soluble cationic or amphoteric polymers in automatic dishwashing detergent composi-

tion is described to prevent or mitigate the tarnishing of silver. The polymers are soluble or dispersible to at least 0.01% by weight in distilled water at 25°C.

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Description**Field of the Invention**

5 The present invention is in the field of machine dishwashing. More specifically, the invention encompasses automatic dishwashing detergents or rinse aids in granular, liquid, gel, solid and tablet form which contain a cationic or amphoteric water soluble polymer to prevent or reduce the tarnishing of silver.

Background of the Invention

10 Tarnishing of silver, sometimes referred to as discoloring, is caused by contact of silver with food containing sulphur compounds (e.g. eggs, onions and mustard).

Silver tarnishing can also occur when oxygen bleaching agents used in machine dish washing compositions oxidize the silver to black silver oxide.

15 The problem of tarnishing has been addressed in WO 95/10588 (Unilever) which describes bleaching machine dish wash compositions containing nitrogen containing heterocyclic compounds.

Antitarnish compounds including water-soluble bismuth compounds such as bismuth nitrate are disclosed in GB 2,297,096 and EP 0 636 688. GB 2,283,494 discloses formulations containing heavy metals which are also said to prevent silver tarnishing as are paraffin oil; and non-paraffin oil organic agents as claimed in EP 0 690 122.

20 It is an object of the present invention to provide compositions, suitable for use in machine dishwashing methods, which prevent the tarnishing of silver while at the same time maintaining good cleaning performance towards soiled articles.

Description of the Invention

25 Accordingly the present invention describes the use of a water-soluble cationic or amphoteric polymer in a machine dish wash composition to prevent or reduce the tarnishing of silver.

The present application also relates to a machine dish wash composition comprising a water soluble cationic polymer comprising as a monomer an ionene group and a builder.

30 Also described is a rinse aid for use in a dish washing machine comprising a water soluble cationic polymer comprising as a monomer an ionene group and water.

It is expected that the wash pH at which this invention would be employed would either naturally fall within the pH range 6-11 or, optionally, would be buffered in that range.

The wash pH of the rinse cycle is thought to be in the region of 4 -8.

Detailed Description of the Invention**Water Soluble Cationic or Amphoteric Polymer**

40 The present composition contains as essential components a water soluble cationic or amphoteric polymer.

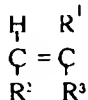
In the context of this specification "water soluble" polymers are polymers which, because of their molecular weight or monomer composition, are soluble or dispersible to at least the extent of 0.01% by weight in distilled water at 25°C.

"Cationic" polymers herein comprise polymers in which at least one of the monomer units making up the polymer contains a cationic charge. It is preferred if the cationic charge is sustained over a portion of the wash pH range of pH

45 6 to pH 11, those monomer units not containing cationic charges being nonionic in nature. "Amphoteric" polymers herein are defined as polymers in which at least one of the comprising monomer units contains a cationic charge preferably over a portion of the pH range 6-11 and at least one of the comprising monomer units contains an anionic charge over the same portion of the pH range 6-11. The overall composition of an amphoteric polymer can otherwise

freely be chosen from among monomers containing cationic charge(s), monomers containing anionic charge(s), monomer units containing both cationic and anionic charge(s), and monomer units which are nonionic in nature.

50 Preferred monomers useful in this invention may be represented structurally as unsaturated compounds as in formula I.



wherein R¹ is hydrogen, hydroxyl, or a C₁ to C₃₀ straight or branched alkyl radical; R² is hydrogen, or a C₁₋₃₀ straight or branched alkyl, a C₁₋₃₀ straight or branched alkyl substituted aryl, aryl substituted C₁₋₃₀ straight or branched alkyl radical, or a poly oxyalkene condensate of an aliphatic radical; and R³ is a heteroatomic alkyl or aromatic radical containing either one or more quaternized nitrogen atoms or one or more amine groups which possess a positive charge over a portion of the pH interval pH 6 to 11. Such amine groups can be further delineated as having a pK_a of about 6 or greater, as defined by R. Laughlin in "Cationic Surfactants, Physical Chemistry", edited by D.N. Rubingh and P.M. Holland, Marcel Dekker, New York, 1991, ISBN 0-8247-8357-3.

Especially preferred are the ionene class of internal cationic monomers as defined by D. R. Berger in "Cationic Surfactants, Organic Chemistry", edited by J.M. Richmond, Marcel Dekker, New York, 1990, ISBN 0-8247-8381-6, herein incorporated by reference. This class includes co-poly ethylene imine, co-poly ethoxylated ethylene imine and co-poly quaternized ethoxylated ethylene imine; co-poly [(dimethylimino) trimethylene (dimethylimino) hexamethylene disalt], co-poly [(diethylimino) trimethylene (dimethylimino) trimethylene disalt]; co-poly [(dimethylimino) 2-hydroxypropyl salt]; co-polyquaternium-2, co-polyquaternium-17, and co-polyquaternium 18, as defined in the "International Cosmetic Ingredient Dictionary, 5th Edition", edited by J.A. Wenninger and G.N. McEwen.

Especially preferred is the cationic polymer based on polyethylene imine.

The counterion of the comprising cationic co-monomer is freely chosen from the halides: chloride, bromide, and iodide; or from hydroxide, phosphate, sulfate, hydrosulfate, ethyl sulfate, methyl sulfate, formate, and acetate.

It is understood that the polymers in this invention may be incorporated into the dishwasher at any point in the wash process. An effective amount of said polymer is 0.025 to 5.00 grams, preferably 0.1 to 3.00 grams, most preferably 0.2 to 2.50 grams per wash cycle, all by weight. If the polymer is incorporated into a typical concentrated detergent formulation, this effective amount is equivalent to a polymer concentration of 0.1 to 20.0%, preferably 0.4 to 12.0%, and most preferably 0.8 to 10.0% by weight of the formulation. In a typical rinse aid composition, this effective amount is equivalent to a polymer concentration of 0.5 to 90.0%, preferably 2.0 to 60.0%, and most preferably 4.0 to 50.0% by weight of the formulation.

It is preferred if the polymers have a molecular weight ranging from 1000 to 10⁶, the preferred molecular weight range depends on the polymer composition. For the cationic polymers based on polyethylene imine, the preferred molecular weight range is from 6,000 to 1,000,000, with the range from 10,000 to 100,000 being especially preferred.

Builder

The compositions of the invention may contain a builder. The builder may be a phosphate or non-phosphate builder.

Compositions of the invention comprising a water-soluble phosphate builder typically contain this builder at a level of from 1 to 90% by weight, preferably from 10 to 80% by weight, most preferably from 20 to 70% by weight of the composition. Specific examples of water-soluble phosphate builders are the alkali metal triphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid. Sodium or potassium triphosphate is most preferred.

The compositions of the present invention may comprise a water-soluble nonphosphate builder. This is typically present at a level of from 1 to 90% by weight, preferably from 10 to 80% by weight, most preferably from 20 to 70% by weight of the composition. Suitable examples of non-phosphorus-containing inorganic builders include water-soluble alkali metal carbonates, bicarbonates, sesquicarbonates, borates, silicates, including layered silicates such as SKS-6 ex. Hoechst, metasilicates, and crystalline and amorphous aluminosilicates. Specific examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates, silicates including layered silicates and zeolites.

Organic detergent builders can also be used as nonphosphate builders in the present invention. Examples of organic builders include alkali metal citrates, succinates, malonates, fatty acid sulfonates, fatty acid carboxylates, nitrilotriacetates, oxydisuccinates, alkyl and alkenyl disuccinates, oxydiacetates, carboxymethyloxy succinates, ethylenediamine tetraacetates, tartrate monosuccinates, tartrate disuccinates, tartrate monoacetates, tartrate diacetates, oxidized starches, oxidized heteropolymeric polysaccharides, polyhydroxysulfonates, polycarboxylates such as polyacrylates, polymaleates, polyacetates, polyhydroxyacrylates, polyacrylate/polymaleate and polyacrylate/ polymethacrylate copolymers, acrylate/maleate/vinyl alcohol terpolymers, aminopolycarboxylates and polyacetal carboxylates, and

polyaspartates and mixtures thereof. Such carboxylates are described in U.S. Patent Nos. 4,144,226, 4,146,495 and 4,686,062. Alkali metal citrates, nitrilotriacetates, oxydisuccinates, acrylate/maleate copolymers and acrylate/maleate/vinyl alcohol terpolymers are especially preferred nonphosphate builders.

Optional Ingredients

In addition to the essential ingredients described herein above, the compositions of the invention may be formulated as detergent compositions comprising conventional ingredients, preferably selected from enzymes, buffering systems, oxygen bleaching systems, surfactants, heavy metal ion sequestrants, antiscalants, corrosion inhibitors, and antifoams.

Enzymes

Enzymes capable of facilitating the removal of soils from a substrate may also be present in a combined amount of up to about 10% by weight of active enzyme. Such enzymes include proteases, amylases, lipases, esterases, cellulases, pectinases, lactases and peroxidases as conventionally incorporated into detergent compositions.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase and Esperase from Novo Industries A/S (Denmark); and those sold by Genencor International under the tradename Purafect OxP. Preferred commercially available amylases include those - amylases sold under the tradenames Termamyl and Duramyl from Novo Industries and those sold by Genencor International under the tradename Purafect OxAm. A preferred lipase is commercially available from Novo Industries under the trade name Lipolase.

Buffering System

The buffering system may be present in order to deliver a pH of about 6 to about 11 in the wash water. Materials which may be selected for the buffering system include water-soluble alkali metal carbonates, bicarbonates, sesquicarbonates, borates, silicates, layered silicates such as SKS-6 ex Hoechst, metasilicates, phytic acid, citric acid, borate and crystalline and amorphous aluminosilicates and mixtures thereof. Preferred examples include sodium and potassium carbonate, sodium and potassium bicarbonates, borates and silicates, including layered silicates.

Oxygen Bleaching Systems

The present invention may optionally contain an oxygen bleach source chosen from the following:

Peroxy Bleaching Agents - The oxygen bleaching agents of the compositions include organic peroxy acids and diacylperoxides.

Typical monoperoxy acids useful herein include alkyl peroxy acids and aryl peroxy acids such as:

- i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g., peroxy-alpha-naphthoic acid, and magnesium monoperoxyphthalate
- ii) aliphatic and substituted aliphatic monoperoxy acids, e.g., peroxy lauric acid, peroxy stearic acid, epsilon-phthalimido-peroxyhexanoic acid and o-carboxybenzamide peroxyhexanoic acid, N-nonylamidoperadipic acid and N-nonylamidopersuccinic acid.
- iii) Cationic peroxyacids such as those described in U.S. 5,422,028, 5,294,362; and 5,292,447, Oakes et al., U.S. S/N 08/738,504; and U.S. S/N 08/210,973, Oakes et al., herein incorporated by reference.
- iv) Sulfonyl peroxyacids such as compounds described in U.S. 5,039,447 (Monsanto Co.), herein incorporated by reference.

Typical diperoxy acids useful herein include alkyl diperoxy acids and aryl diperoxy acids, such as:

- v) 1,12-diperoxydodecanedioic acid
- vi) 1,9-diperoxyazelaic acid
- vii) diperoxybrassylic acid; diperoxysecacic acid and diperoxy-isophthalic acid
- viii) 2-decyldiperoxybutan-1,4-dioic acid
- ix) N,N-terephthaloyl-di(6-aminopercaproic acid).

A typical diacylperoxide useful herein includes dibenzoylperoxide.

Inorganic peroxygen compounds are also suitable for the present invention. Examples of these materials useful in the invention are salts of monopersulfate, perborate monohydrate, perborate tetrahydrate, and percarbonate.

Preferred peroxy bleaching agents include epsilon-phthalimidoperoxyhexanoic acid, o-carboxybenzamidoperox-

hexanoic acid, and mixtures thereof.

The organic or inorganic peroxy acid is present in the composition in an amount such that the level of peroxy acid in the wash solution is about 1 ppm to about 300 ppm AvOx, preferably about 2 ppm to about 200 ppm AvOx.

The oxygen bleaching agent may be incorporated directly into the formulation or may be encapsulated by any number of encapsulation techniques.

A preferred encapsulation method is described in U.S. Patent No. 5,200,236 issued to Lang et al., herein incorporated by reference. In the patented method, the bleaching agent is encapsulated as a core in a paraffin wax material having a melting point from about 40°C to 50°C. The wax coating has a thickness of from 100 to 1500 microns.

Bleach Precursors - Suitable peracid precursors for peroxy bleach compounds have been amply described in the literature, including GB Nos. 836,988; 855,735; 907,356; 907,358; 907,950; 1,003,310 and 1,246,339; U.S. Patent Nos. 3,332,882 and 4,128,494.

Typical examples of precursors are polyacylated alkylene diamines, such as N,N,N',N'-tetraacetylene diamine (TAED) and N,N,N',N'-tetraacetylmethylene diamine (TAMD); acylated glycolurils, such as tetraacetylglycoluril (TAGU); triacetylcyanurate, sodium sulfophenyl ethyl carbonic acid ester, sodium acetyloxybenzene sulfonate (SABS), sodium nonanoyloxy benzene sulfonate (SNOBS) and choline sulfophenyl carbonate. Peroxybenzoic acid precursors are known in the art, e.g., as described in GB-A-836,988. Examples of suitable precursors are phenylbenzoate; phenyl p-nitrobenzoate; o-nitrophenyl benzoate; o-carboxyphenyl benzoate; p-bromophenylbenzoate; sodium or potassium benzoyloxy benzene-sulfonate; and benzoic anhydride.

Preferred peroxygen bleach precursors are sodium p-benzoyloxybenzene sulfonate, N,N,N',N'-tetraacetylene diamine, sodium nonanoyloxybenzene sulfonate and choline sulfophenyl carbonate.

The peroxygen bleach precursors are present in the composition in an amount from about 1 to about 20 weight percent, preferably from about 1 to about 15 wt. %, most preferably from about 2 to about 15 wt. %. To deliver a functional peroxygen bleach from a precursor, a source of hydrogen peroxide is required. The hydrogen peroxide source is preferably a compound that delivers hydrogen peroxide on dissolution. Preferred sources of hydrogen peroxide are sodium perborate, either as the mono- or tetrahydrate and sodium percarbonate. The source of hydrogen peroxide, when included in these compositions is present at a level of about 1% to about 40% by weight, preferably from about 2% to about 30% by weight, most preferably from about 4% to about 25% by weight.

Bleach Catalyst - An effective amount of a bleach catalyst can also be present in the invention. A number of organic catalysts are available such as the sulfonimines as described in U.S. Patents 5,041,232; 5,047,163 and 5,463,115.

Transition metal bleach catalysts are also useful, especially those based on manganese, iron, cobalt, titanium, molybdenum, nickel, chromium, copper, ruthenium, tungsten and mixtures thereof. These include simple water-soluble salts such as those of iron, manganese and cobalt as well as catalysts containing complex ligands.

Suitable examples of manganese catalysts containing organic ligands are described in U.S. Pat. 4,728,455, U.S. Pat. 5,114,606, U.S. Pat. 5,153,161, U.S. Pat. 5,194,416, U.S. Pat. 5,227,084, U.S. Pat. 5,244,594, U.S. Pat. 5,246,612, U.S. Pat. 5,246,621, U.S. Pat. 5,256,779, U.S. Pat. 5,274,147, U.S. Pat. 5,280,117 and European Pat. App. Pub. Nos. 544,440, 544,490, 549,271 and 549,272. Preferred examples of these catalysts include $\text{Mn}^{\text{IV}}_2(\text{u-O})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$, $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-triazacyclononane})_4(\text{ClO}_4)_4$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_3$, $\text{Mn}^{\text{IV}}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})\text{-(OCH}_3)_3(\text{PF}_6)$, and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611.

Iron and manganese salts of aminocarboxylic acids in general are useful herein including iron and manganese aminocarboxylate salts disclosed for bleaching in the photographic color processing arts. A particularly useful transition metal salt is derived from ethylenediaminedisuccinate and any complex of this ligand with iron or manganese.

Another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water soluble complex of manganese (II), (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Preferred ligands include sorbitol, iditol, dulcitol, mannitol, xylitol, arabitol, adonitol, meso-erythritol, meso-inositol, lactose and mixtures thereof. Especially preferred is sorbitol.

U.S. Patent No. 5,114,611 teaches a bleach catalyst comprising a complex of transition metals, including manganese, cobalt, iron or copper with a non-(macro)-cyclic ligand. Other examples include Mn gluconate, $\text{Mn}(\text{CF}_3\text{SO}_3)_2$, and binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including $[\text{bipy}_2\text{Mn}^{\text{III}}(\text{u-O})_2\text{Mn}^{\text{IV}}\text{bipy}_2](\text{ClO}_4)_3$.

Other bleach catalysts are described, for example, in European Pat. App. Pub. Nos. 408,131 (cobalt complexes), 384,503 and 306,089 (metallo-porphyrins), U.S. Pat. 4,728,455 (manganese/multidentate ligand), U.S. Pat. 4,711,748 (adsorbed manganese on aluminosilicate), U.S. Pat. 4,601,845 (aluminosilicate support with manganese, zinc or magnesium salt), U.S. Pat. 4,626,373 (manganese/ligand), U.S. Pat. 4,119,557 (ferric complex), U.S. Pat. 4,430,243 (Chelants with manganese cations and non-catalytic metal cations), and U.S. Pat. 4,728,455 (manganese gluconates).

Useful catalysts based on cobalt are described in Pat. App. Pub. Nos. WO 96/23859, WO 96/23860 and WO 96/23861 and U.S. Pat. 5,559,261. WO 96/23860 describe cobalt catalysts of the type $[\text{CO}_n\text{L}_m\text{X}_p]^z\text{Y}_z$, where L is an

organic ligand molecule containing more than one heteroatom selected from N, P, O and S; X is a co-ordinating species; n is preferably 1 or 2; m is preferably 1 to 5; p is preferably 0 to 4 and Y is a counterion. One example of such a catalyst is N,N'-Bis(salicylidene)ethylenediaminecobalt (II). Other cobalt catalysts described in these applications are based on Co(III) complexes with ammonia and mon-, bi-, tri- and tetradentate ligands such as $[\text{Co}(\text{NH}_3)_5\text{OAc}]^{2+}$ with Cl^- , OAc^- , PF_6^- , SO_4^{2-} , and BF_4^- anions.

Certain transition-metal containing bleach catalysts can be prepared in the situ by the reaction of a transition-metal salt with a suitable chelating agent, for example, a mixture of manganese sulfate and ethylenediaminedisuccinate. Highly colored transition metal-containing bleach catalysts may be co-processed with zeolites to reduce the color impact.

When present, the bleach catalyst is typically incorporated at a level of about 0.0001 to about 10% by wt., preferably about 0.001 to about 5% by weight.

Surfactants

Optionally, a surfactant selected from the list including anionic, nonionic, cationic, amphoteric, and zwitterionic surfactants and mixtures of these surface active agents may be included in the machine dishwashing formulation. Such surfactants are well known in the detergent arts and are described at length in "Surface Active Agents and Detergents", Vol. 2 by Schwartz, Perry and Birch, Interscience Publishers, Inc., 1959, herein incorporated by reference.

Preferred surfactants are one or a mixture of:

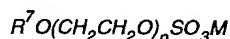
Anionic surfactants - Anionic synthetic detergents can be broadly described as surface active compounds with one or more negatively charged functional groups. An important class of anionic compounds are the water-soluble salts, particularly the alkali metal salts, of organic sulfur reaction products having in their molecular structure an alkyl radical containing from about 6 to 24 carbon atoms and a radical selected from the group consisting of sulfonic and sulfuric acid ester radicals.

Primary Alkyl Sulfates



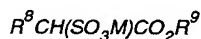
where R^7 is a primary alkyl group of 8 to 18 carbon atoms and M is a solubilizing cation. The alkyl group R^7 may have a mixture of chain lengths. It is preferred that at least two-thirds of the R^7 alkyl groups have a chain length of 8 to 14 carbon atoms. This will be the case if R^7 is coconut alkyl, for example. The solubilizing cation may be a range of cations which are in general monovalent and confer water solubility. An alkali metal, notably sodium, is especially envisaged. Other possibilities are ammonium and substituted ammonium ions, such as trialkanolammonium or trialkylammonium.

Alkyl Ether Sulfates



where R^7 is a primary alkyl group of 8 to 18 carbon atoms, n has an average value in the range from 1 to 6 and M is a solubilizing cation. The alkyl group R^7 may have a mixture of chain lengths. It is preferred that at least two-thirds of the R^7 alkyl groups have a chain length of 8 to 14 carbon atoms. This will be the case if R^7 is coconut alkyl, for example. Preferably n has an average value of 2 to 5.

Fatty Acid Ester Sulfonates



where R^8 is an alkyl group of 6 to 16 atoms, R^9 is an alkyl group of 1 to 4 carbon atoms and M is a solubilizing cation. The group R^9 may have a mixture of chain lengths. Preferably at least two-thirds of these groups have 6 to 12 carbon atoms. This will be the case when the moiety $R^8 \text{CH}(-) \text{CO}_2(-)$ is derived from a coconut source, for instance. It is preferred that R^9 is a straight chain alkyl, notably methyl or ethyl.

Alkyl Benzene Sulfonates



where R^{10} is an alkyl group of 8 to 18 carbon atoms, Ar is a benzene ring (C_6H_4) and M is a solubilizing cation. The group R^{10} may be a mixture of chain lengths. Straight chains of 11 to 14 carbon atoms are preferred.

Paraffin sulfonates having 8 to 22 carbon atoms, preferably 12 to 16 carbon atoms, in the alkyl moiety. These surfactants are commercially available as Hostapur SAS from Hoechst Celanese.

Olefin sulfonates having 8 to 22 carbon atoms, preferably 12 to 16 carbon atoms. U.S. Patent No. 3,332,880 contains a description of suitable olefin sulfonates.

Organic phosphate based anionic surfactants include organic phosphate esters such as complex mono- or diester phosphates of hydroxyl- terminated alkoxide condensates, or salts thereof. Included in the organic phosphate esters are phosphate ester derivatives of polyoxyalkylated alkylaryl phosphate esters, of ethoxylated linear alcohols and ethoxylates of phenol. Also included are nonionic alkoxylates having a sodium alkylencarboxylate moiety linked to a terminal hydroxyl group of the nonionic through an ether bond. Counterions to the salts of all the foregoing may be those of alkali metal, alkaline earth metal, ammonium, alkanolammonium and alkylammonium types.

Particularly preferred anionic surfactants are the fatty acid ester sulfonates with formula:



where the moiety $R^8CH(-)CO_2(-)$ is derived from a coconut source and R^9 is either methyl or ethyl; primary alkyl sulfates with the formula:



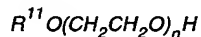
wherein R^7 is a primary alkyl group of 10 to 18 carbon atoms and M is a sodium cation; and paraffin sulfonates, preferably with 12 to 16 carbon atoms to the alkyl moiety.

Nonionic surfactants - Nonionic surfactants can be broadly defined as surface active compounds with one or more uncharged hydrophilic substituents. A major class of nonionic surfactants are those compounds produced by the condensation of alkylene oxide groups with an organic hydrophobic material which may be aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements. Illustrative, but not limiting examples, of various suitable nonionic surfactant types are:

polyoxyalkene condensates of aliphatic carboxylic acids, whether linear- or branched-chain and unsaturated or saturated, especially ethoxylated and/or propoxylated aliphatic acids containing from about 8 to about 18 carbon atoms in the aliphatic chain and incorporating from about 2 to about 50 ethylene oxide and/or propylene oxide units. Suitable carboxylic acids include "coconut" fatty acids (derived from coconut oil) which contain an average of about 12 carbon atoms, "tallow" fatty acids (derived from tallow-class fats) which contain an average of about 18 carbon atoms, palmitic acid, myristic acid, stearic acid and lauric acid,

polyoxyalkene condensates of aliphatic alcohols, whether linear- or branched-chain and unsaturated or saturated, especially ethoxylated and/or propoxylated aliphatic alcohols containing from about 6 to about 24 carbon atoms and incorporating from about 2 to about 50 ethylene oxide and/or propylene oxide units. Suitable alcohols include "coconut" fatty alcohol, "tallow" fatty alcohol, lauryl alcohol, myristyl alcohol and oleyl alcohol.

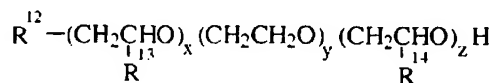
Ethoxylated fatty alcohols may be used alone or in admixture with anionic surfactants, especially the preferred surfactants above. The average chain lengths of the alkyl group R^{11} in the general formula:



is from 6 to 20 carbon atoms. Notably the group R^{11} may have chain lengths in a range from 9 to 18 carbon atoms.

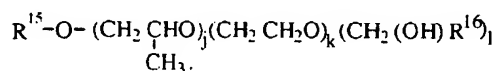
The average value of n should be at least 2. The numbers of ethylene oxide residues may be a statistical distribution around the average value. However, as is known, the distribution can be affected by the manufacturing process or altered by fractionation after ethoxylation. Particularly preferred ethoxylated fatty alcohols have a group R^{11} which has 9 to 18 carbon atoms while n is from 2 to 8.

Also included within this category are nonionic surfactants having a formula:



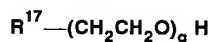
wherein R^{12} is a linear alkyl hydrocarbon radical having an average of 6 to 18 carbon atoms, R^{13} and R^{14} are each linear alkyl hydrocarbons of about 1 to about 4 carbon atoms, x is an integer of from 1 to 6, y is an integer of from 4 to 20 and z is an integer from 4 to 25.

One preferred nonionic surfactant of the above formula is Poly-Tergent SLF-18 a registered trademark of the Olin Corporation, New Haven, Conn. having a composition of the above formula where R^{12} is a C_8 - C_{10} linear alkyl mixture, R^{13} and R^{14} are methyl, x averages 3, y averages 12 and z averages 16. Another preferred nonionic surfactant is:



wherein R^{15} is a linear, aliphatic hydrocarbon radical having from about 4 to about 18 carbon atoms including mixtures thereof; and R^{16} is a linear, aliphatic hydrocarbon radical having from about 2 to about 26 carbon atoms including mixtures thereof; j is an integer having a value of from 1 to about 3; k is an integer having a value from 5 to about 30; and l is an integer having a value of from 1 to about 3. Most preferred are compositions in which j is 1, k is from about 10 to about 20 and l is 1. These surfactants are described in NO 94/22800. Other preferred nonionic surfactants are linear fatty alcohol alkoxylates with a capped terminal group, as described in U.S. 4,340,766 to BASF. Particularly preferred is Plurafac LF403 ex. BASF.

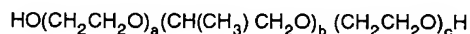
Another nonionic surfactant included within this category are compounds of formula:



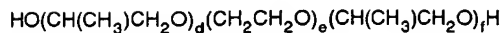
wherein R^{17} is a C_6 - C_{24} linear or branched alkyl hydrocarbon radical and q is a number from 2 to 50; more preferably R^{17} is a C_8 - C_{18} linear alkyl mixture and q is a number from 2 to 15.

polyoxyethylene or polyoxypropylene condensates of alkyl phenols, whether linear- or branched-chain and unsaturated or saturated, containing from about 6 to 12 carbon atoms and incorporating from about 2 to about 25 moles of ethylene oxide and/or propylene oxide. Poxyoxyethylene derivatives of sorbitan mono-, di-, and tri-fatty acid esters wherein the fatty acid component has between 12 and 24 carbon atoms. The preferred polyoxyethylene derivatives are of sorbitan monolaurate, sorbitan trilaurate, sorbitan monopalmitate, sorbitan tripalmitate, sorbitan monostearate, sorbitan monoisostearate, sorbitan tristearate, sorbitan monooleate, and sorbitan trioleate. The polyoxyethylene chains may contain between about 4 and 30 ethylene oxide units, preferably about 10 to 20. The sorbitan ester derivatives contain 1, 2 or 3 polyoxyethylene chains dependent upon whether they are mono-, di- or tri-acid esters.

polyoxyethylene-polyoxypropylene block copolymers having the formula:

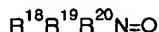


or



wherein a, b, c, d, e and f are integers from 1 to 350 reflecting the respective polyethylene oxide and polypropylene oxide blocks of said polymer. The polyoxyethylene component of the block polymer constitutes at least about 10% of the block polymer. The material preferably has a molecular weight of between about 1,000 and 15,000, more preferably from about 1,500 to about 6,000. These materials are well-known in the art. They are available under the trademark "Pluronic" and "Pluronic R", a product of BASF Corporation.

Amine oxides having formula:

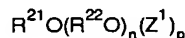


wherein R^{18} , R^{19} and R^{20} are saturated aliphatic radicals or substituted saturated aliphatic radicals. Preferable amine oxides are those wherein R^{18} is an alkyl chain of about 10 to about 20 carbon atoms and R^{19} and R^{20} are methyl or ethyl groups or both R^{18} and R^{19} are alkyl chains of about 6 to about 14 carbon atoms and R^{20} is a methyl or ethyl group.

Amphoteric synthetic detergents - can be broadly described as derivatives of aliphatic tertiary amines, in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contain from about 8 to about 18 carbons and one contains an anionic water-solubilizing group, i.e., carboxy, sulpho, sulphato, phosphato or phosphono. Examples of compounds falling within this definition are sodium 3-dodecylamino propionate and sodium 2-dodecylamino propane sulfonate.

Zwitterionic synthetic detergents - can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium and sulphonium compounds in which the aliphatic radical may be straight chained or branched, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulpho, sulphato, phosphato or phosphono. These compounds are frequently referred to as betaines. Besides alkyl betaines, alkyl amino and alkyl amido betaines are encompassed within this invention.

Alkyl Glycosides



wherein R^{21} is a monovalent organic radical (e.g., a monovalent saturated aliphatic, unsaturated aliphatic or aromatic radical such as alkyl, hydroxyalkyl, alkenyl, hydroxyalkenyl, aryl, alkylaryl, hydroxyalkylaryl, arylalkyl, alkenylaryl, arylalkenyl, etc.) containing from about 6 to about 30 (preferably from about 8 to 18 and more preferably from about 9 to about 13) carbon atoms; R^{22} is a divalent hydrocarbon radical containing from 2 to about 4 carbon atoms such as ethylene, propylene or butylene (most preferably the unit $(\text{R}^{22}\text{O})_n$ represents repeating units of ethylene oxide, propylene oxide and/or random or block combinations thereof); n is a number having an average value of from 0 to about 12; Z^1 represents a moiety derived from a reducing saccharide containing 5 or 6 carbon atoms (most preferably a glucose unit); and p is a number having an average value of from 0.5 to about 10 preferably from about 0.5 to about 5.

Examples of commercially available materials from Henkel Kommanditgesellschaft Aktien of Dusseldorf, Germany include APG 300, 325 and 350 with R^{21} being $\text{C}_9\text{-C}_{11}$, n is 0 and p is 1.3, 1.6 and 1.8-2.2 respectively; APG 500 and 550 with R^{21} is $\text{C}_{12}\text{-C}_{13}$, n is 0 and p is 1.3 and 1.8-2.2, respectively; and APG 600 with R^{21} being $\text{C}_{12}\text{-C}_{14}$, n is 0 and p is 1.3.

While esters of glucose are contemplated especially, it is envisaged that corresponding materials based on other reducing sugars, such as galactose and mannose are also suitable.

Particularly preferred nonionic surfactants are polyoxyethylene and polyoxypropylene condensates of linear aliphatic alcohols.

The preferred range of surfactant is from about 0.5 to 30 % by wt., more preferably from about 0.5 to 15% by weight of the composition.

Sequestrants

The detergent compositions herein may also optionally contain one or more transition metal chelating agents. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove

iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetraacetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexaacetates, diethylenetriaminepentaacetates, ethylenediamine disuccinate, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) and diethylenetriaminepentakis (methylenephosphonates). Preferably, these amino phosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent No. 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 5.0% by weight of such composition.

Anti-Scalants

Scale formation on dishes and machine parts can be a significant problem. It can arise from a number of sources but, primarily it results from precipitation of either alkaline earth metal carbonates, phosphates or silicates. Calcium carbonate and phosphates are the most significant problem. To reduce this problem, ingredients to minimize scale formation can be incorporated into the composition. These include polyacrylates of molecular weight from 1,000 to 400,000 examples of which are supplied by Rohm & Haas, BASF and Alco Corp. and polymers based on acrylic acid combined with other moieties. These include acrylic acid combined with maleic acid, such as Sokalan CP5 and CP7 supplied by BASF or Acusol 479N supplied by Rohm & Haas; with methacrylic acid such as Colloid 226/35 supplied by Rhone-Poulenc; with phosphonate such as Casi 773 supplied by Buckman Laboratories; with maleic acid and vinyl acetate such as polymers supplied by Hnls; with acrylamide; with sulfophenol methallyl ether such as Aquatreat AR 540 supplied by Alco; with 2-acrylamido-2-methylpropane sulfonic acid such as Acumer 3100 supplied by Rohm & Haas or such as K-775 supplied by Goodrich; with 2-acrylamido-2-methylpropane sulfonic acid and sodium styrene sulfonate such as K-798 supplied by Goodrich; with methyl methacrylate, sodium methallyl sulfonate and sulfophenol methallyl ether such as Alcoperse 240 supplied by Alco; polymaleates such as Belcene 200 supplied by FMC; polymethacrylates such as Tamol 850 from Rohm & Haas; Polyaspartates; ethylenediamine disuccinate; organo polyphosphonic acids and their salts such as the sodium salts of aminotri(methylenephosphonic acid) and ethane 1-hydroxy-1,1-diphosphonic acid. The anti-scalant, if present, is included in the composition from about 0.05% to about 10% by weight, preferably from 0.1% to about 5% by weight, most preferably from about 0.2% to about 5% by weight.

Corrosion inhibitors

The composition may optionally contain other corrosion inhibitors to reduce the tarnishing of silver flatware. Such inhibitors include benzotriazole and other members of the azole family. Particularly preferred are azoles, including imidazoles. Additional antitarnish additives include water-soluble bismuth compounds such as bismuth nitrate as taught in GB 2,297,096 A; heavy metal salts of copper, iron, manganese, zinc, or titanium (EP 0 636 688 A1, GB 2,283,494 A); paraffin oil; and non-paraffin oil organic agents such as fatty esters of mono or polyhydric alcohols as claimed in EP 0 690 122 A2.

Antifoams

The compositions of the present invention, when formulated for use in machine dishwashing compositions, preferably comprise an antifoam system. Suitable antifoam systems for use herein may comprise essentially any known antifoam compound, including, for example, silicone antifoams, silicone oil, mono- and di-alkyl acid phosphates, mineral oil, and 2-alkyl and alkanol antifoam compounds. Even if the machine dishwashing composition contains only defoaming surfactants, the antifoam assists to minimize foam which food soils can generate. The compositions may include 0.02 to 2% by weight of antifoam, preferably, 0.05 to 1.0%. Preferred antifoam systems are described in Angevaere et al.; U.S. Serial No. 08/539,923, incorporated herein by reference.

Form of the Composition

The machine dish treatment compositions of the present invention can be formulated in any desirable form such

as powders, granulates, pastes, liquids, gels, solids or tablets. As an example, the process of preparing a granulate may involve preparing a slurry of the ingredients identified above and drying the mixture by means of suitable equipment such as a turbine dryer (Turbogranulation dryer ex Vomm-Turbo Technology, Vomm Impianti E Processi SrL, Milan, Italy). Also, the process may involve preparing the slurry, spray-drying the slurry by conventional techniques using a spray tower in which the slurry is atomized and dried in a hot air stream, followed by restructuring the resulting powder, optionally after milling, in a granulation process (L 3 dige recycler and L 3 dige plow shear). In a particularly favorable process, the slurry is sprayed onto fine (recycled) particles and then dried to form gradually growing co-granules. Another attractive possibility is to dry the slurry in a rotary drum granulator and to spray slurry onto recirculated fines, thus building up coarser particles. These particles are either simultaneously or subsequently dried to give a co-granule with a more homogeneous moisture distribution than those obtained by use of a turbine dryer.

The process of preparing a tablet may involve admixing the ingredients identified above, transferring the mixture to the tablet die, and compressing with a compaction pressure from about 3×10^6 kg/m² to about 3×10^7 kg/m². It may be preferable to pre-granulate some or all of the ingredients, optionally with surfactant to enhance dissolution, to give granulates of size 100-2000 microns and mix these together with any remaining material prior to compaction. Another possibility is to precoat the granulate with any liquid component of the composition via, for example, a fluid bed, pan coater or rolling drum to give encapsulates. The encapsulates are then compressed with a compaction pressure from about 1×10^6 kg/m² to about 3×10^7 kg/m².

Machine Dishwashing Method

A preferred machine dishwashing method comprises treating soiled articles selected from crockery, glassware, hollowware, silverware and cutlery and mixtures thereof, with an aqueous solution having dissolved or dispensed therein an effective amount of a machine dishwashing composition in accord with the invention. By an effective amount of the machine dishwashing composition it is meant from 8 g to 60 g of the composition dissolved or dispersed in a wash solution of volume from 3 to 10 liters, as typical product dosages and wash solution volumes commonly employed in conventional machine dishwashing methods.

The following examples will serve to distinguish this invention from the prior art and illustrate its embodiment more fully. Unless indicated otherwise, all parts, percentages and portions referred to are by weight.

Example 1

Machine dishwashing detergent formulations were prepared as detailed below. Example A is a granular product based on sodium perborate monohydrate and tetraacetyl ethylene diamine as the bleach system and delivering a wash pH of 10.0. Examples B and C are also granular products but employ N-phthaloylamino-peroxycaproic acid as the bleach and yield a pH of 8.5 in the wash. Example B represents conventional technology while examples A and C are in accord with the present invention.

COMPONENT	Example A	Example B	Example C
Sodium tripolyphosphate	50.0	62	62
Acrylate homopolymer ¹	----	2.5	2.5
Acrylate / maleate copolymer ²	----	2.5	2.5
Amorphous sodium silicate (SiO ₂ :Na ₂ O = 2)	7.0	----	----
Sodium carbonate	10.0	----	----
Sodium bicarbonate	----	12.7	12.7
Sodium perborate monohydrate	10.0	----	----
Tetraacetyl ethylene diamine	2.0	----	----

¹Sokalan PA25 ex BASF

²Sokalan CP5 ex BASF

(continued)

COMPONENT	Example A	Example B	Example C
N-phthaloylamino-peroxycaproic acid ³	----	2.8	2.8
Anionic surfactant ⁴	----	7.6	7.6
Solid ketone particles dispersed in an organic carrier ⁵	----	1.0	1.0
Polybutadiene ⁶	----	0.3	0.3
Nonionic surfactant ⁷	0.75	----	----
Poly (ethyleneimine) ⁸	2.5	----	2.5
Enzymes	2.0	5.0	5.0
Water and minor components	to 100	to 100	to 100

³Ex Ausimont⁴Alpha Step ML 40 ex Henkel⁵Dehypon 2429 ex Henkel⁶ex Elf Atochem⁷LF 403 ex BASF⁸50-100,000 MW ex PolySciences (catalog # 06090)**Example 2**

The inhibitory effect on silver tarnishing of the polymeric materials claimed for this invention is demonstrated in this example. The silver tarnishing observed during machine dishwashing with Example C defined above was compared with that obtained with the conventional technology Example B. A fifteen wash-cycle procedure was employed which consisted of loading a Miele Super-Electronic G 595 SC machine dishwasher such that four 8 ounce drinking glasses were placed in the upper rack, two 8 inch dinner plates were placed on the lower rack and two of each of Onieda 'Seneca' silver plated spoons, forks, and knives were loaded into the cutlery basket. The Universal 65 °C washing program was selected and the wash program executed using soft water (< 10 ppm calcium expressed as CaCO₃) and 18 grams of the machine dishwashing composition comprising Example B or Example C. Each set of wash articles was put through fifteen consecutive cycles with the same formulation, after which time the silver articles were removed and graded for silver tarnishing. The grading was performed by two expert appraisers on each article and the results were averaged together. Grading was through visual inspection according to the following six point scale:

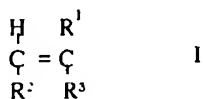
- 0 = no tarnish (shiny silver)
- 1 = very slightly tarnished (light golden color)
- 2 = slightly tarnished (medium golden color)
- 3 = tarnished (very dark golden color)
- 4 = very tarnished (grey coating)
- 5 = severely tarnished (dark grey coating)
- 6 = very severely tarnished (black coating)

grade (0-6 scale)	knife	fork	spoon
Example B	1	4	3
Example C	0.5	0.5	0.5

As the above results clearly show, the formulation comprising Example C, which is an embodiment of the present invention, effectively controls the silver tarnishing which is otherwise objectionable in the control (Example B).

Claims

1. Use of a water-soluble cationic or amphoteric polymer in a machine dish wash composition to prevent or reduce the tarnishing of silver.
2. Use of a water-soluble cationic polymer according to claim 1, in which the cationic polymer comprises at least 1 monomer unit having a cationic charge over a portion of the pH range 6-11.
3. Use of a water-soluble cationic polymer according to claim 1 or claim 2, in which the cationic polymer comprises at least 1 monomer unit having formula (I)



wherein R¹ is hydrogen, hydroxyl, or a C₁ to C₃₀ straight or branched alkyl radical; R² is hydrogen, a C₁ to C₃₀ straight or branched alkyl, a C₁ to C₃₀ straight or branched alkyl substituted aryl, aryl substituted C₁ to C₃₀ straight or branched alkyl radical or a poly oxyalkene condensate of an aliphatic radical, and R³ is a heteroatomic alkyl or aromatic radical containing either one or more quaternized nitrogen atoms or one or more amine groups.

4. Use of a water-soluble cationic polymer according to claim 1 or 2 in which the cationic monomer is based on an ionene group.
5. Use of a water soluble cationic polymer according to any claim 1, 2 or 4 in which the cationic polymer is polyethylene imine.
6. A machine dish wash composition comprising a water soluble cationic polymer comprising as a monomer an ionene group and a builder.
7. A rinse aid for use in a dish washing machine comprising a water soluble cationic polymer comprising as a monomer an ionene group and water.
8. A machine dish wash composition according to claim 6 in which the level of water soluble polymer is from 0.1 to 20 wt % of the total composition.
9. A machine dish wash composition according to claim 6 or claim 8 which further comprises an oxygen containing bleaching agent or precursor thereof.
10. A rinse aid composition according to claim 7 in which the level of water soluble polymer is from 2 to 60 wt % of the total composition.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 30 5467

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	DE 195 32 542 A (HENKEL KGAA) 6 March 1997 * claim 5; examples 1,3 *	6-8,10	C11D3/37 C11D3/00
X	GB 2 172 607 A (DIVERSEY CORP) 24 September 1986 * page 6, line 24 - line 27; example 20 *	7,10	
A	EP 0 541 475 A (VIKING INDUSTRIES) 12 May 1993 * page 4, line 4 - page 5, line 9; claims 1-9 *	1-10	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C11D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24 November 1998	Examiner Ainscow, J
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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